

An ether extract/concentrate of a commercial liquid smoke solution was fractionated by preparative gas-liquid chromatography. Sensory evaluation indicated a fraction to be slightly smoky. Another smoke concentrate obtained by adsorption of the liquid smoke solution on an activated carbon column

and desorption with acetone was fractionated in a similar fashion. Sensory evaluation using paired comparison and ranking tests indicated a fraction to be as "smoky" as the solution from which it was derived. This fraction having the essential smoke flavor contains primarily phenols and carbonyls.

Although many studies have been reported on the composition of wood smoke, the individual components responsible for the characteristic flavor and aroma of smoked products are still unknown. Attempts to identify these components by fractionating the smoke samples into acidic-, phenolic-, carbonyl-, and neutral-containing classes of compounds have had only partial success. The resolution among classes of compounds achieved by chemical separations is not sufficient to rule out contamination of a fraction by extraneous compounds.

While it has been claimed that phenols, as a class, are of primary importance in the characterization of smoke flavor (Bratzler *et al.*, 1969; Tilgner *et al.*, 1962), another report (Wasserman, 1966) suggested that a mixture of three phenols, rated as "smoky" by a taste panel, did not reproduce smoke aroma and flavor exactly. The characteristic smoky flavor does not appear to be limited to one class of compounds; it is probably a blend of a number of chemicals belonging to different classes of compounds. Spanyol *et al.* (1966) prepared smoke solutions of different compositions based on information obtained by gas-liquid chromatography of smoke preparations. The compounded solutions, however, did not have an aroma and flavor like the original preparations. While Spanyol's approach was more logical than those of previous methods, his lack of success in reproducing smoke flavor may have been due to insufficient information about the composition of the smoke preparations.

We have identified a number of constituents of smoke condensates (Doerr *et al.*, 1966; Fiddler *et al.*, 1966) and solutions (Fiddler *et al.*, 1970). On the basis of this information we are reporting a procedure for the preparation of liquid smoke concentrates, their fractionation by gas-liquid chromatography, and sensory evaluation of these fractions.

EXPERIMENTAL

Preparation of Smoke Flavor Concentrate. The starting material for the smoke flavor fractionations was CharSol (C-6), a commercial liquid smoke solution obtained from the Red Arrow Products Corp., Milwaukee, Wis. The method of preparation of this product has been described in a patent (Hollenbeck, 1963).

A smoke concentrate was prepared from an ether extract of the C-6 solution, as reported previously (Fiddler *et al.*, 1970).

A second concentrate was prepared by the adsorption of smoke components on activated charcoal, then desorption with acetone. A column consisting of 10 g dry 70- to 80-

mesh Anasorb, an activated coconut charcoal obtained from Analabs, Inc., Hamden, Conn., was prepared in a 50-ml buret. Thirty-five ml of the smoke solution C-6 was applied to the column in 5-ml portions, and 2-ml fractions of the effluent were collected. Each fraction was subjected to aroma characterization and gas chromatographic examination. No smoky aroma was noted in the eluate. The column was allowed to drain and nitrogen under pressure was applied to the head of the column to remove as much of the residual water as possible. The adsorbed organic material was then eluted with 50 ml acetone which was evaporated under a stream of nitrogen. The level of concentration of organic material was limited by the amount of residual water in the charcoal column.

Gas-Liquid Chromatography. Analytical gas-liquid chromatographic studies of the smoke concentrates were conducted under conditions described previously (Fiddler *et al.*, 1966, 1970). Fractions for sensory evaluation were selected by smelling the components as they emerged from the gas chromatograph.

Preparative fractionation of the smoke concentrates was carried out with an Aerograph Model A-700 thermal conductivity gas chromatograph using a 6-ft by 1/4-in. o.d. column packed with 30% Carbowax 20M-TPA on 60- to 80-mesh Gas Chrom P. The column was heated from 80° to 170° C at ca. 8° C per min with a helium carrier flow of 200 cc per min. The injection port and detector temperatures were 225° and 250° C, respectively.

Sample Preparations. Quantities of the fractions to be tested were collected and then diluted with distilled water to the same concentration in which they are present in the original CharSol (C-6) solution.

Evaluation of the flavor of the various fractions was carried out by means of frankfurters, prepared according to a standard formulation. The franks were dipped into solutions of the fractions for approximately 15 sec, then cooked in a commercial smokehouse according to a 90-min heating program.

Sensory Evaluation Tests. The taste panel consisted of approximately 30 members of the laboratory who have been testing frankfurters for about a year. The franks were cooked in boiling water for 3 min, then kept warm in double boiler pans filled with hot water. One-inch pieces of frankfurters were served to the members of the panel. The paired comparison test, in which the panelists were requested to select the smokier of a pair of samples, was the principal method of analysis. However, in some tests the panelists were asked to rate their choice of smokier sample for degree of smokiness on a 7-point scale: 0—not smokier; 1 and 2—slightly more smoky; 3 and 4—moderately more smoky; and 5 and 6—considerably more smoky than the other member of the pair.

Table I. Sensory Evaluation

	Paired Comparison Test ^a	Degree of Smokiness ^b	
		Total	Mean
Smoke Solution C-6	15	32	2.1
Acetone Concentrate	12	29	2.4
Smoke Solution C-6	15	40	2.6
Fraction B	10	36	3.6
Acetone Concentrate	12	22	1.8
Fraction B	14	37	2.6

^a Number of panelists selecting the sample as smokier of the pair.
^b Ranking on a 7-point scale where: 0—not smokier; 1 and 2—slightly more smoky; 3 and 4—moderately more smoky; 5 and 6—considerably more smoky than the other member of the pair.

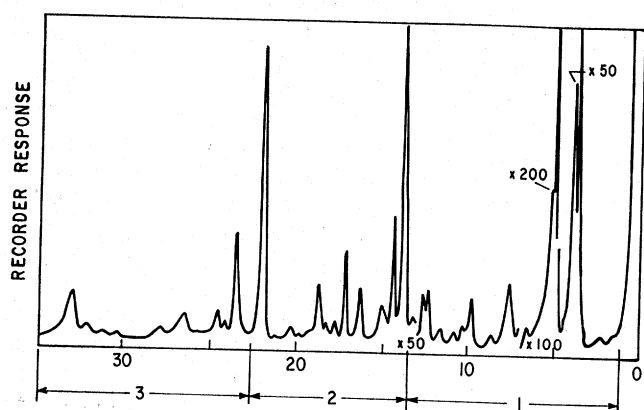


Figure 1. Gas-liquid chromatogram indicating the three fractions of the liquid smoke solution ether extract

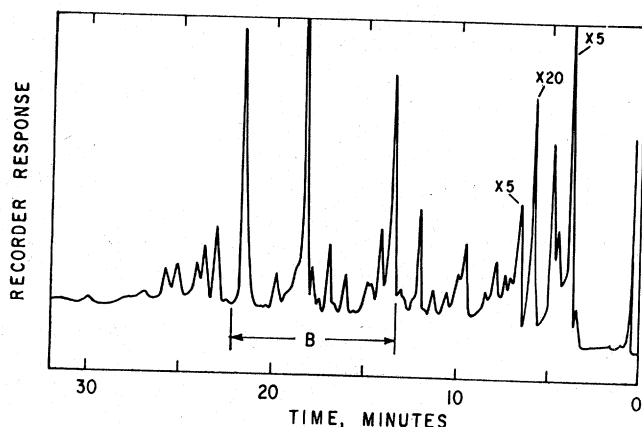


Figure 2. Gas-liquid chromatogram of the concentrate obtained by adsorption-desorption of the smoke solution on activated charcoal indicating "smoky" fraction B

The paired comparison data were analyzed for degree of statistical significance by means of the tables of Amerine *et al.* (1965). The values for the degree of smokiness are given as both the totals and the means.

RESULTS AND DISCUSSION

In initial studies to characterize smoke flavor, an ether extract of C-6 solution, in which 48 components had been identified previously (Fiddler *et al.*, 1970) was used. Based on some preliminary evaluations, this preparation was separated into three fractions shown in Figure 1. Fraction 1 contained low boiling compounds up to but not including cyclotene; Fraction 2 included the components from cyclotene to syringol; Fraction 3 consisted of the higher boiling compounds. Taste panel studies with frankfurters showed the original C-6

smoke solution was smokier than the ether extract or any of the fractions. While fraction 2 was significantly less smoky than the C-6 solution, it was considerably more smoky than either of the other two fractions. Further studies on the flavor imparted by mixing the various fractions were not pursued because of the difficulty in obtaining sufficient material by preparative gas chromatography for testing.

All of the simple aliphatic acids previously identified in smoke preparations are in fraction 1 and impart very little smoky flavor to the franks. This is in agreement with the work reported by Bratzler *et al.* (1969). However, the acids may be important in the smoke process for other reasons such as: denaturing the meat protein to form the "skin," increasing the peelability of the casing with sausage products, aiding in surface color development, serving as a solvent for smoke components, and acting as modifiers of other smoke flavor components either directly or at subthreshold levels.

One factor responsible for the difference in smokiness between ether extract, fraction 2, and C-6 smoke solution may be the absence from the ether extract of several components that are present in the original smoke solution. These became evident in the C-6 solution after the ether extraction of components having the same glc retention times. Infrared studies of the residual components in the extracted C-6 indicated they are mixtures of carbonyl compounds, probably polyfunctional components of poor ether solubility. These carbonyl components have a caramel or "burnt" sugar aroma, and might have an important modifying effect on the flavor produced by the phenols in fraction 2. The carbonyl compounds remaining in the C-6 residue after ether extraction are present in addition to the cyclic carbonyl and dicarbonyl compounds that were reported in the ether extract (Fiddler *et al.*, 1970).

In our original studies many of these carbonyl compounds were not found in the smoke condensates prepared in our laboratory (Fiddler *et al.*, 1966). The difference in flavor produced by the smoke condensates and the C-6 liquid smoke solution may be due to the modifying effect of the carbonyls, which results in a "smoky" rather than a harsh "phenolic" or "creosotic" character.

Since it appeared that the ether insoluble components of the liquid smoke solution might be important in imparting a "smoky" flavor to frankfurters, other methods of separation such as distillation, chemical fractionation, and column chromatography with various resins and gels were investigated. The most promising method at this time is the use of activated charcoal to remove components from the smoke solution. The color- and aroma-containing material was adsorbed on the charcoal and was initially eluted with methanol. Methanol has good solvent properties for the more polar compounds and is miscible with water; however, it has been shown to react with the acids present in the smoke solution to form esters and impart a sweet note to the aroma (Doerr *et al.*, 1966). Acetone was then substituted to elute the organic material from the charcoal. The glc profile of the concentrate obtained by acetone desorption of charcoal is shown in Figure 2. This concentrate appears identical to the original smoke solution except for several small peaks from the latter that are so volatile they elute in the first few minutes under the gas chromatographic conditions used. The acetone concentrate was fractionated into three fractions similar to the ether extract concentrate by preparative glc. Results of sensory evaluation of franks treated with fraction B, the acetone concentrate, and the smoke solution C-6 are shown in Table I.

Fraction B-treated franks were selected as being the smokier of the pair as often as those treated with the acetone concentrate. Frankfurters treated with fraction B or the acetone concentrate were chosen almost as frequently as those treated with the original smoke solution C-6. There was no statistically significant difference in the number of times the panel members selected each treatment as the smokier of a pair. However, when the degree of smokiness of the smokier member of each pair was rated, fraction B treatment showed a greater amount of smokiness than the smoke solution C-6 or the acetone concentrate from which it was prepared.

It is apparent that fraction B contains the essential components of smoke flavor. To date the following compounds have been identified in this fraction: unsubstituted, 4-methyl-, 4-ethyl-, 4-propyl-, and 4-vinylguaiacols, eugenol, syringol, phenol, *ortho*-, *meta*-, and *para*-cresols, 4-ethylphenol, 3,4-, 2,4-, and/or 2,5-xilenols, 3-methyl-, 3-ethyl-, and 3,4-dimethyl-2-cyclopenten-2-ol-1-ones, tiglic acid, maltol, and 2,5 dimethyl-4-hydroxy-3(2H)furanone. Further fractionation and more intensive study of the components in the flavor fraction from the acetone concentrate of the liquid smoke adsorbed on charcoal may aid in elucidating the composition of smoke flavor.

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